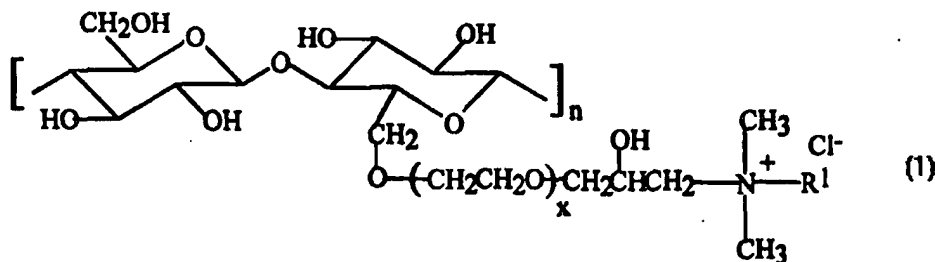




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : A61K 7/06	A1	(11) International Publication Number: WO 99/02122 (43) International Publication Date: 21 January 1999 (21.01.99)
(21) International Application Number: PCT/US97/12281 (22) International Filing Date: 9 July 1997 (09.07.97) (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): YANG, Jian-Zhong [CN/JP]; 2-1-215-727, Koyo-cho, Naka 1-chome, Higashinada-ku, Kobe 658 (JP). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.

(54) Title: HAIR CARE COMPOSITION COMPRISING HYDROPHOBICALLY MODIFIED CATIONIC CELLULOSE



(57) Abstract

Disclosed is a hair care composition comprising by weight: (a) from about 0.01 % to about 10 % of a hydrophobically modified cationic cellulose having formula (1), wherein R^1 is an alkyl having from about 8 to about 22 carbons, n is an integer from 1 to about 1250; x is 0 or an integer from 1 to about 6; and having a molecular weight of no more than about 250,000; from about 0.01 % to about 20 % of a viscosifying agent selected from the group consisting of a gel network, a conditioning polymer, a hair fixative polymer, and mixtures thereof; and (c) an aqueous carrier.

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HAIR CARE COMPOSITION COMPRISING HYDROPHOBICALLY MODIFIED CATIONIC CELLULOSE

5

TECHNICAL FIELD

The present invention relates to a hair care composition containing a hydrophobically modified cationic cellulose having a certain molecular weight
10 which provides good conditioning benefit.

BACKGROUND

Scalp and hair become soiled due to their contact with the surrounding environment and from sebum secreted from the hair follicles. The build-up of sebum and environmental soiling can cause the hair to have a dirty or greasy
15 feel, and an unattractive appearance. In order to ameliorate these effects, it is necessary to shampoo the hair with regularity.

Shampooing the hair removes excess sebum and other environmental soiling but has disadvantages in that the hair can be left in a wet, tangled, and relatively unmanageable state. Shampooing can also result in the hair becoming
20 dry due to the removal of natural oils or other hair moisturizing materials. After shampooing, the hair can also suffer from a perceived loss of "softness." Frequent shampooing also contributes to the phenomena of "split ends," particularly for long hair. Split ends refers to a condition wherein the ends of the hair are split into two or more shafts, resulting in a frizzy appearance.

25 A variety of approaches have been developed to condition the hair. These range from post-shampooing hair rinses, to leave-on hair conditioners, to the inclusion of hair conditioning components in shampoos. When these hair conditioning compositions are formulated as shampoos and conditioners, they typically have a thickened product form, such as a gel or cream, for ease of
30 application to the hair. When these hair conditioning compositions are formulated as mousses and hair sprays, they typically further contain a hair fixative polymer to provide hair styling benefits.

Hydrophobically modified cationic celluloses such as Polyquaternium-24 are known in the art as hair conditioning agents which provide smoothness and
35 softness to the hair, such as in Japanese Patent Laid-open publications S61-

181801 and H7-304637. An example of a suitable Polyquaternium-24 polymer is that with tradename QUATERISOFT POLYMER LM-200 supplied by Amerchol.

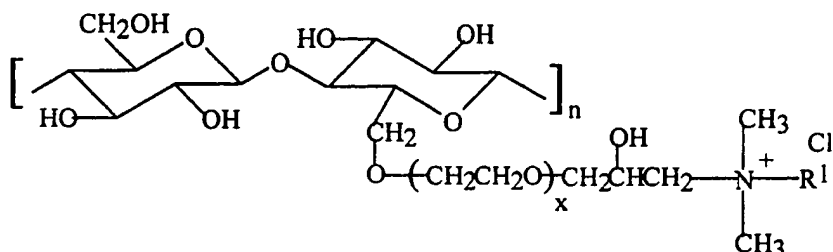
Hair conditioning compositions in the form of shampoos and conditioners have conventionally been based on the combination of a cationic surfactant, such as a quaternary ammonium compound, in combination with solid aliphatic compounds such as fatty alcohols. These combinations generally result in a gel-network structure which provides the compositions with a thick, creamy texture and thus makes the composition easy to be applied to the hair. However, when hydrophobically modified cationic celluloses of high molecular weight are added to these product forms, these compounds build up with the gel-network to make the formulation so viscous that it provides negative sticky feeling to the hair. In addition, viscous formulations are difficult to process. Hair conditioning compositions in the form of mousses and hair sprays typically further contain a hair fixative polymer to provide hair styling benefits. However, when hydrophobically modified cationic celluloses of high molecular weight are added to these product forms, these compounds build up with the hair fixative polymers, particularly those with anionic and/or hydrophobic moieties, and the formulation becomes so viscous it cannot be dispensed from packages used for mousses and hair sprays.

Based on the foregoing, there is a need for a hair conditioning composition which can include hydrophobically modified cationic celluloses in combination with components which viscosify the composition to provide preferable conditioning benefits. None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

The present invention is directed to a hair care composition comprising by weight:

- (a) from about 0.01% to about 10% of a hydrophobically modified cationic cellulose having the following formula:



wherein R¹ is an alkyl having from about 8 to about 22 carbons, n is an integer from 1 to about 1250; x is 0 or an integer from 1 to about 6; and having a molecular weight of no more than about 250,000;

- 5 (b) from about 0.01% to about 20% of a viscosifying agent selected from the group consisting of a gel network, a hair conditioning polymer, a hair fixative polymer, and mixtures thereof; and
- (c) an aqueous carrier.

These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure.

DETAILED DESCRIPTION

While the specification concludes with claims particularly pointing and distinctly claiming the invention, it is believed the present invention will be better understood from the following description.

All percentages are by weight of the total composition unless otherwise indicated. All ratios are weight ratios unless otherwise indicated. All percentages, ratios, and levels of ingredients referred to herein are based on the actual amount of the ingredient, and do not include solvents, fillers, or other materials with which the ingredient may be combined as commercially available products, unless otherwise indicated.

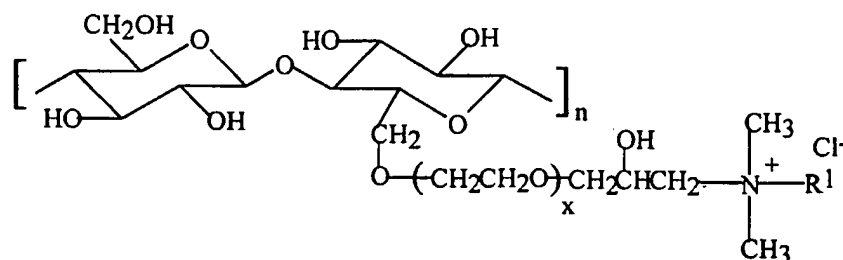
As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

25 All cited references are incorporated herein by reference in their entireties. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

HYDROPHOBICALLY MODIFIED CATIONIC CELLULOSE

The hair care composition of the present invention comprises by weight from about 0.01% to about 10%, preferably from about 0.1% to about 5%, more preferably from about 0.5% to about 3% of a hydrophobically modified cationic cellulose having low molecular weight.

The low molecular weight hydrophobically modified cationic celluloses useful in the present invention are those having the following formula:



wherein R^1 is an alkyl having from about 8 to about 22 carbons, preferably from about 10 to about 18 carbons; n is an integer from 1 to about 1250, preferably from about 4 to about 500; and x is 0 or an integer from 1 to about 6, preferably 1 to 3. The hydrophobically modified cationic celluloses useful in the present invention must have a molecular weight of no more than about 250,000, preferably from about 800 to about 100,000. The 3% aqueous solution of such hydrophobically modified cationic cellulose has a viscosity of no more than about 200cps, preferably from about 2 to about 100cps.

Hydrophobically modified cationic celluloses of the present invention provide many benefits to hair care compositions over the conventionally used high molecular weight hydrophobically modified cationic celluloses. Hydrophobically modified cationic celluloses of the present invention are compatible with gel networks and conditioning polymers which are included in shampoo and conditioner compositions to provide favorable conditioning and texture. Hydrophobically modified cationic celluloses of the present invention are compatible with hair fixative polymers which are included in hair styling compositions to provide styling benefits. Hydrophobically modified cationic celluloses of the present invention are further easier to dissolve upon formulation into various hair care compositions as mentioned herein. Thus, these hydrophobically modified cationic celluloses can be incorporated into a wide variety of hair care compositions and provide conditioning benefits such as softness, smoothness, slick feel, and ease of combing. Thus, hydrophobically modified cationic celluloses of the present invention can be incorporated into a wide variety of hair care compositions with ordinary processes known to one skilled in the art.

VISCOSIFYING AGENT

The hair care composition of the present invention comprises by weight from about 0.1% to about 20% of a viscosifying agent selected from the group consisting of a gel network, a conditioning polymer, a hair fixative polymer, and

mixtures thereof. When the hair care composition is a shampoo or conditioning composition, the gel network and/or the conditioning polymer is preferably comprised, and the hair fixative polymer is optionally comprised. When the hair care composition is a hair spray or mousse composition, the hair fixative polymer is preferably comprised, and the conditioning polymer is preferably comprised.

Gel Network

The gel network useful herein is made of a solid aliphatic compound and a cationic surfactant. The shampoo and conditioner compositions of the present invention preferably include by weight from about 0.01% to about 19.9%, preferably from about 0.1% to about 10% of the solid aliphatic compound, and from about 0.01% to about 10%, preferably from about 0.1% to about 4% of the cationic surfactant.

Solid Aliphatic Compound

The solid aliphatic compound useful herein are those having a melting point of at least about 25°C selected from the group consisting of fatty alcohols, fatty acids, fatty alcohol derivatives, fatty acid derivatives, hydrocarbons, steroids, and mixtures thereof. It is understood by the artisan that some fatty alcohol derivatives can also be classified as fatty acid derivatives. However, a given classification is not intended to be a limitation on that particular compound, but is done so for convenience of classification and nomenclature. Further, it is understood by the artisan that, depending on the number and position of double bonds, and length and position of the branches, certain compounds having certain required carbon atoms may have a melting point of less than about 25°C. Such compounds of low melting point are not intended to be included in this section.

The fatty alcohols useful herein are those having from about 14 to about 30 carbon atoms, preferably from about 16 to about 22 carbon atoms. These fatty alcohols can be straight or branched chain alcohols and can be saturated or unsaturated. Nonlimiting examples of fatty alcohols include, cetyl alcohol, stearyl alcohol, behenyl alcohol, and mixtures thereof.

The fatty acids useful herein are those having from about 10 to about 30 carbon atoms, preferably from about 12 to about 22 carbon atoms, and more preferably from about 16 to about 22 carbon atoms. These fatty acids can be straight or branched chain acids and can be saturated or unsaturated. Also included are diacids, triacids, and other multiple acids which meet the

requirements herein. Also included herein are salts of these fatty acids. Nonlimiting examples of fatty acids include lauric acid, palmitic acid, stearic acid, behenic acid, sebacic acid, and mixtures thereof.

The fatty alcohol derivatives and fatty acid derivatives useful herein
5 include alkyl ethers of fatty alcohols, alkoxylated fatty alcohols, alkyl ethers of
alkoxylated fatty alcohols, esters of fatty alcohols, fatty acid esters of compounds
having esterifiable hydroxy groups, hydroxy-substituted fatty acids, and mixtures
thereof. Nonlimiting examples of fatty alcohol derivatives and fatty acid
10 derivatives include materials such as methyl stearyl ether; the ceteth series of
compounds such as ceteth-1 through ceteth-45, which are ethylene glycol ethers
of cetyl alcohol, wherein the numeric designation indicates the number of
ethylene glycol moieties present; the steareth series of compounds such as
steareth-1 through 10, which are ethylene glycol ethers of steareth alcohol,
15 wherein the numeric designation indicates the number of ethylene glycol
moieties present; cetareth 1 through cetareth-10, which are the ethylene
glycol ethers of cetareth alcohol, i.e. a mixture of fatty alcohols containing
predominantly cetyl and stearyl alcohol, wherein the numeric designation
indicates the number of ethylene glycol moieties present; C₁-C₃₀ alkyl ethers of
20 the ceteth, steareth, and cetareth compounds just described; polyoxyethylene
ethers of behenyl alcohol; ethyl stearate, cetyl stearate, cetyl palmitate, stearyl
stearate, myristyl myristate, polyoxyethylene cetyl ether stearate,
polyoxyethylene stearyl ether stearate, polyoxyethylene lauryl ether stearate,
ethyleneglycol monostearate, polyoxyethylene monostearate, polyoxyethylene
distearate, propyleneglycol monostearate, propyleneglycol distearate,
25 trimethylolpropane distearate, sorbitan stearate, polyglyceryl stearate, glyceryl
monostearate, glyceryl distearate, glyceryl tristearate, and mixtures thereof.

Hydrocarbons useful herein include compounds having at least about 20
carbons.

Steroids useful herein include compounds such as cholesterol.

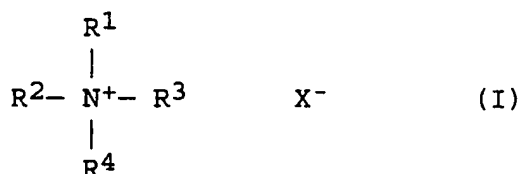
30 Solid aliphatic compounds of a single compound of high purity are
preferred. Single compounds of pure fatty alcohols selected from the group of
pure cetyl alcohol, stearyl alcohol, and behenyl alcohol are highly preferred. By
"pure" herein, what is meant is that the compound has a purity of at least about
90%, preferably at least about 95%. These single compounds of high purity

provide good rinsability from the hair when the consumer rinses off the composition.

Commercially available solid aliphatic compounds useful herein include: cetyl alcohol, stearyl alcohol, and behenyl alcohol having tradenames KONOL series available from New Japan Chemical (Osaka, Japan), and NAA series available from NOF (Tokyo, Japan); pure behenyl alcohol having tradename 1-DOCOSANOL available from WAKO (Osaka, Japan), various fatty acids having tradenames NEO-FAT available from Akzo (Chicago Illinois, USA), HYSTRENE available from Witco Corp. (Dublin Ohio, USA), and DERMA available from Vevy (Genova, Italy); and cholesterol having tradename NIKKOL AGUASOME LA available from Nikko.

Cationic Surfactant

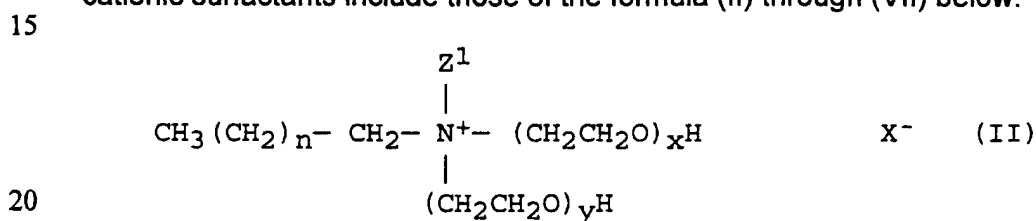
The cationic surfactants useful herein include those corresponding to the general formula (I):



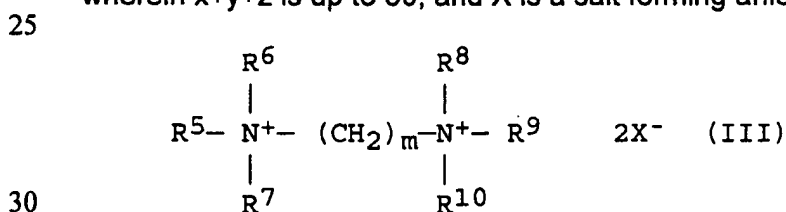
wherein at least one of R^1 , R^2 , R^3 , and R^4 is selected from an aliphatic group of from 8 to 30 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms, the remainder of R^1 , R^2 , R^3 , and R^4 are independently selected from an aliphatic group of from 1 to about 22 carbon atoms or an aromatic, alkoxy, polyoxyalkylene, alkylamido, hydroxyalkyl, aryl or alkylaryl group having up to about 22 carbon atoms; and X is a salt-forming anion such as those selected from halogen, (e.g. chloride, bromide), acetate, citrate, lactate, glycolate, phosphate, nitrate, sulfonate, sulfate, alkylsulfate, and alkyl sulfonate radicals. The aliphatic groups can contain, in addition to carbon and hydrogen atoms, ether linkages, and other groups such as amino groups. The longer chain aliphatic groups, e.g., those of about 12 carbons, or higher, can be saturated or unsaturated. Preferred is when R^1 , R^2 , R^3 , and R^4 are independently selected from C_1 to about C_{22} alkyl. Nonlimiting examples of cationic surfactants useful include the materials having the following CTFA designations: quaternium-8, quaternium-24, quaternium-26, quaternium-27, quaternium-30, quaternium-33,

quaternium-43, quaternium-52, quaternium-53, quaternium-56, quaternium-60, quaternium-62, quaternium-70, quaternium-72, quaternium-75, quaternium-77, quaternium-78, quaternium-80, quaternium-81, quaternium-82, quaternium-83, quaternium-84, and mixtures thereof.

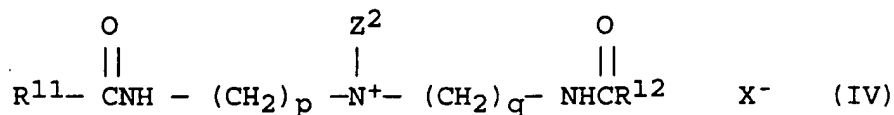
- 5 Also preferred are hydrophilically substituted cationic surfactants in which at least one of the substituents contain one or more aromatic, ether, ester, amido, or amino moieties present as substituents or as linkages in the radical chain, wherein at least one of the $R^1 - R^4$ radicals contain one or more hydrophilic moieties selected from alkoxy (preferably $C_1 - C_3$ alkoxy),
 10 polyoxyalkylene (preferably $C_1 - C_3$ polyoxyalkylene), alkylamido, hydroxyalkyl, alkylester, and combinations thereof. Preferably, the hydrophilically substituted cationic surfactant contains from 2 to about 10 nonionic hydrophile moieties located within the above stated ranges. Preferred hydrophilically substituted cationic surfactants include those of the formula (II) through (VII) below:



wherein n is from 8 to about 28, x+y is from 2 to about 40, Z^1 is a short chain alkyl, preferably a $C_1 - C_3$ alkyl, more preferably methyl, or $-(CH_2CH_2O)_zH$ wherein x+y+z is up to 60, and X is a salt forming anion as defined above;



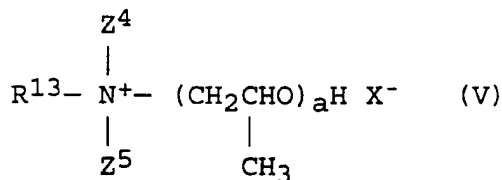
wherein m is 1 to 5, one or more of R^5 , R^6 , and R^7 are independently an $C_1 - C_{30}$ alkyl, the remainder are $-CH_2CH_2OH$, one or two of R^8 , R^9 , and R^{10} are independently an $C_1 - C_{30}$ alkyl, and remainder are $-CH_2CH_2OH$, and X is a
 35 salt forming anion as mentioned above;





wherein Z^2 is an alkyl, preferably a $C_1 - C_3$ alkyl, more preferably methyl, and
 5 Z^3 is a short chain hydroxyalkyl, preferably hydroxymethyl or hydroxyethyl, p and
 q independently are integers from 2 to 4, inclusive, preferably from 2 to 3,
 inclusive, more preferably 2, R^{11} and R^{12} , independently, are substituted or
 unsubstituted hydrocarbyls, preferably $C_{12} - C_{20}$ alkyl or alkenyl, and X is a salt
 forming anion as defined above;

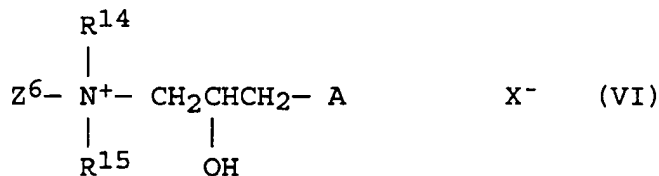
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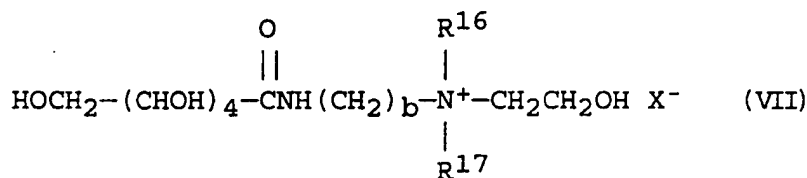
wherein R^{13} is a hydrocarbyl, preferably a $C_1 - C_3$ alkyl, more preferably methyl,
 Z^4 and Z^5 are, independently, short chain hydrocarbyls, preferably $C_2 - C_4$ alkyl
 or alkenyl, more preferably ethyl, a is from 2 to about 40, preferably from about 7
 20 to about 30, and X is a salt forming anion as defined above;

25



wherein R^{14} and R^{15} , independently, are $C_1 - C_3$ alkyl, preferably methyl, Z^6 is
 a $C_{12} - C_{22}$ hydrocarbyl, alkyl carboxy or alkylamido, and A is a protein,
 30 preferably a collagen, keratin, milk protein, silk, soy protein, wheat protein, or
 hydrolyzed forms thereof; and X is a salt forming anion as defined above;

35



wherein b is 2 or 3, R^{16} and R^{17} , independently are $C_1 - C_3$ hydrocarbyls
 40 preferably methyl, and X is a salt forming anion as defined above. Nonlimiting

examples of hydrophilically substituted cationic surfactants useful include the materials having the following CTFA designations: quaternium-16, quaternium-61, quaternium-71, quaternium-79 hydrolyzed collagen, quaternium-79 hydrolyzed keratin, quaternium-79 hydrolyzed milk protein, quaternium-79 hydrolyzed silk, quaternium-79 hydrolyzed soy protein, and quaternium-79 hydrolyzed wheat protein. Highly preferred compounds include commercially available materials of the following tradenames; VARIQUAT K1215 and 638 from Witco Chemical, MACKPRO KLP, MACKPRO WLW, MACKPRO MLP, MACKPRO NSP, MACKPRO NLW, MACKPRO WWP, MACKPRO NLP, MACKPRO SLP from McIntyre, ETHOQUAD 18/25, ETHOQUAD O/12PG, ETHOQUAD C/25, ETHOQUAD S/25, and ETHODUOQUAD from Akzo, DEHYQUAT SP from Henkel, and ATLAS G265 from ICI Americas.

Salts of primary, secondary, and tertiary fatty amines are also suitable cationic surfactants. The alkyl groups of such amines preferably have from about 12 to about 22 carbon atoms, and can be substituted or unsubstituted. Particularly useful are amido substituted tertiary fatty amines. Such amines, useful herein, include stearamidopropyldimethylamine, stearamidopropyldiethylamine, stearamidoethyldiethylamine, palmitamidopropyldimethylamine, palmitamidopropyldiethylamine, palmitamidoethyldiethylamine, behenamidopropyldimethylamine, behenamidopropyldiethylamine, behenamidoethyldiethylamine, arachidamidopropyldimethylamine, arachidamidopropyldiethylamine, arachidamidoethyldiethylamine, diethylaminoethylstearamide. Also useful are dimethylstearamine, dimethylsoyamine, soyamine, myristylamine, tridecylamine, ethylstearylamine, N-tallowpropane diamine, ethoxylated (with 5 moles of ethylene oxide) stearylamine, dihydroxyethylstearylamine, and arachidylbehenylamine. These amines can also be used in combination with acids such as L-glutamic acid, lactic acid, hydrochloric acid, malic acid, succinic acid, acetic acid, fumaric acid, tartaric acid, citric acid, L-glutamic hydrochloride, and mixtures thereof; more preferably L-glutamic acid, lactic acid, citric acid. Cationic amine surfactants included among those useful are disclosed in U.S. Patent 4,275,055, Nachtigal, et al., issued June 23, 1981, which is incorporated by reference herein in its entirety.

The cationic surfactants for use herein may also include a plurality of ammonium quaternary moieties or amino moieties, or a mixture thereof.

Conditioning Polymer

5 The conditioning polymer useful herein is selected from the group consisting of cationic polymers, nonionic polymers, silicone polymers, and mixtures thereof. The shampoo and conditioner compositions of the present invention preferably include by weight from about 0.01% to about 20%, preferably from about 0.1% to about 10% of a conditioning polymer.

Cationic Polymer

10 The cationic polymers useful herein include materials made by polymerization of one type of monomer or made by two (i.e., copolymers) or more types of monomers.

Preferably, the cationic polymer is a water-soluble cationic polymer. By "water soluble" cationic polymer, what is meant is a polymer which is sufficiently
15 soluble in water to form a substantially clear solution to the naked eye at a concentration of 0.1% in water (distilled or equivalent) at 25°C. The preferred polymer will be sufficiently soluble to form a substantially clear solution at 0.5% concentration, more preferably at 1.0% concentration.

The cationic polymers hereof will generally have a weight average
20 molecular weight which is at least about 5,000, typically at least about 10,000, and is less than about 10 million. Preferably, the molecular weight is from about 100,000 to about 2 million. The cationic polymers will generally have cationic nitrogen-containing moieties such as quaternary ammonium or cationic amino moieties, and mixtures thereof.

25 The cationic charge density is preferably at least about 0.1 meq/gram, more preferably at least about 1.5 meq/gram, even more preferably at least about 1.1 meq/gram, still more preferably at least about 1.2 meq/gram. Cationic charge density of the cationic polymer can be determined according to the Kjeldahl Method. Those skilled in the art will recognize that the charge density of
30 amino-containing polymers may vary depending upon pH and the isoelectric point of the amino groups. The charge density should be within the above limits at the pH of intended use.

Any anionic counterions can be utilized for the cationic polymers so long as the water solubility criteria is met. Suitable counterions include halides (e.g.,

Cl, Br, I, or F, preferably Cl, Br, or I), sulfate, and methylsulfate. Others can also be used, as this list is not exclusive.

The cationic nitrogen-containing moiety will be present generally as a substituent, on a fraction of the total monomer units of the cationic hair conditioning polymers. Thus, the cationic polymer can comprise copolymers, 5 terpolymers, etc. of quaternary ammonium or cationic amine-substituted monomer units and other non-cationic units referred to herein as spacer monomer units. Such polymers are known in the art, and a variety can be found in the CTFA Cosmetic Ingredient Dictionary, 3rd edition, edited by Estrin, 10 Crosley, and Haynes, (The Cosmetic, Toiletry, and Fragrance Association, Inc., Washington, D.C., 1982).

Suitable cationic polymers include, for example, copolymers of vinyl monomers having cationic amine or quaternary ammonium functionalities with water soluble spacer monomers such as acrylamide, methacrylamide, alkyl and 15 dialkyl acrylamides, alkyl and dialkyl methacrylamides, alkyl acrylate, alkyl methacrylate, vinyl caprolactone, and vinyl pyrrolidone. The alkyl and dialkyl substituted monomers preferably have C₁ - C₇ alkyl groups, more preferably C₁ - C₃ alkyl groups. Other suitable spacer monomers include vinyl esters, vinyl alcohol (made by hydrolysis of polyvinyl acetate), maleic anhydride, propylene 20 glycol, and ethylene glycol.

The cationic amines can be primary, secondary, or tertiary amines, depending upon the particular species and the pH of the composition. In general, secondary and tertiary amines, especially tertiary amines, are preferred.

Amine-substituted vinyl monomers can be polymerized in the amine form, 25 and then optionally can be converted to ammonium by a quaternization reaction. Amines can also be similarly quaternized subsequent to formation of the polymer. For example, tertiary amine functionalities can be quaternized by reaction with a salt of the formula R'X wherein R' is a short chain alkyl, preferably a C₁ - C₇ alkyl, more preferably a C₁ - C₃ alkyl, and X is an anion which forms a 30 water soluble salt with the quaternized ammonium.

Suitable cationic amino and quaternary ammonium monomers include, for example, vinyl compounds substituted with dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, monoalkylaminoalkyl acrylate, monoalkylaminoalkyl methacrylate, trialkyl methacryloxyalkyl ammonium salt, 35 trialkyl acryloxyalkyl ammonium salt, diallyl quaternary ammonium salts, and

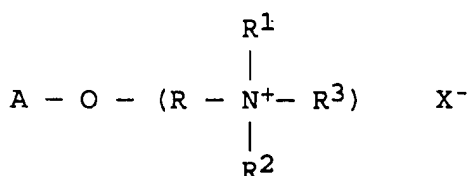
vinyl quaternary ammonium monomers having cyclic cationic nitrogen-containing rings such as pyridinium, imidazolium, and quaternized pyrrolidone, e.g., alkyl vinyl imidazolium, alkyl vinyl pyridinium, alkyl vinyl pyrrolidone salts. The alkyl portions of these monomers are preferably lower alkyls such as the C₁ - C₃ alkyls, more preferably C₁ and C₂ alkyls. Suitable amine-substituted vinyl monomers for use herein include dialkylaminoalkyl acrylate, dialkylaminoalkyl methacrylate, dialkylaminoalkyl acrylamide, and dialkylaminoalkyl methacrylamide, wherein the alkyl groups are preferably C₁ - C₇ hydrocarbyls, more preferably C₁ - C₃, alkyls.

The cationic polymers hereof can comprise mixtures of monomer units derived from amine- and/or quaternary ammonium-substituted monomer and/or compatible spacer monomers.

Suitable cationic hair conditioning polymers include, for example: copolymers of 1-vinyl-2-pyrrolidone and 1-vinyl-3-methylimidazolium salt (e.g., chloride salt) (referred to in the industry by the Cosmetic, Toiletry, and Fragrance Association, "CTFA", as Polyquaternium-16), such as those commercially available from BASF Wyandotte Corp. (Parsippany, NJ, USA) under the LUVIQUAT tradename (e.g., LUVIQUAT FC 370); copolymers of 1-vinyl-2-pyrrolidone and dimethylaminoethyl methacrylate (referred to in the industry by CTFA as Polyquaternium-11) such as those commercially available from Gaf Corporation (Wayne, NJ, USA) under the GAFQUAT tradename (e.g., GAFQUAT 755N); cationic diallyl quaternary ammonium-containing polymers, including, for example, dimethyldiallylammonium chloride homopolymer and copolymers of acrylamide and dimethyldiallylammonium chloride, referred to in the industry (CTFA) as Polyquaternium 6 and Polyquaternium 7, respectively; and mineral acid salts of amino-alkyl esters of homo- and co-polymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms, as described in U.S. Patent 4,009,256, incorporated herein by reference.

Other cationic polymers that can be used include polysaccharide polymers, such as cationic cellulose derivatives and cationic starch derivatives.

Cationic polysaccharide polymer materials suitable for use herein include those of the formula:



5

wherein: A is an anhydroglucose residual group, such as a starch or cellulose anhydroglucose residual, R is an alkylene oxyalkylene, polyoxyalkylene, or hydroxyalkylene group, or combination thereof, R¹, R², and R³ independently
 10 are alkyl, aryl, alkylaryl, arylalkyl, alkoxyalkyl, or alkoxyaryl groups, each group containing up to about 18 carbon atoms, and the total number of carbon atoms for each cationic moiety (i.e., the sum of carbon atoms in R¹, R² and R³) preferably being about 20 or less, and X is an anionic counterion, as previously described.

15 Cationic cellulose is available from Amerchol Corp. (Edison, NJ, USA) in their Polymer JR® and LR® series of polymers, as salts of hydroxyethyl cellulose reacted with trimethyl ammonium substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 10. Another type of cationic cellulose includes the
 20 polymeric quaternary ammonium salts of hydroxyethyl cellulose reacted with lauryl dimethyl ammonium-substituted epoxide, referred to in the industry (CTFA) as Polyquaternium 24. These materials are available from Amerchol Corp. (Edison, NJ, USA) under the tradename Polymer LM-200®.

Other cationic polymers that can be used include cationic guar gum derivatives, such as guar hydroxypropyltrimonium chloride (commercially
 25 available from Celanese Corp. in their Jaguar R series). Other materials include quaternary nitrogen-containing cellulose ethers (e.g., as described in U.S. Patent 3,962,418, incorporated herein by reference), and copolymers of etherified cellulose and starch (e.g., as described in U.S. Patent 3,958,581, incorporated herein by reference.)

30 Nonionic Polymer

Nonionic polymers useful herein include cellulose derivatives, hydrophobically modified cellulose derivatives, ethylene oxide polymers, and ethylene oxide/propylene oxide based polymers. Suitable nonionic polymers are cellulose derivatives including methylcellulose with tradename BENECEL,
 35 hydroxyethyl cellulose with tradename NATROSOL, hydroxypropyl cellulose with tradename KLUCEL, cetyl hydroxyethyl cellulose with tradename POLYSURF 67, all supplied by Hercules. Other suitable nonionic polymers are ethylene

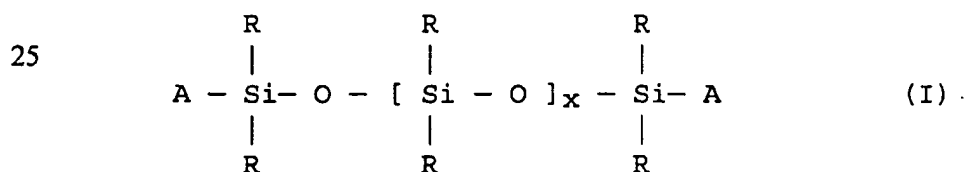
oxide and/or propylene oxide based polymers with tradenames CARBOWAX PEGs, POLYOX WASRs, and UCON FLUIDS, all supplied by Amerchol.

Silicone Polymers

5 Silicone polymers useful herein include those which are volatile soluble or insoluble, or nonvolatile soluble or insoluble. By soluble what is meant is that the silicone polymer is miscible with the carrier of the composition so as to form part of the same phase. By insoluble what is meant is that the silicone polymer forms a separate, discontinuous phase from the carrier, such as in the form of an emulsion or a suspension of droplets of the silicone polymer.

10 The silicone polymers for use herein will preferably have a viscosity of from about 1,000 to about 2,000,000 centistokes at 25°C, more preferably from about 10,000 to about 1,800,000, and even more preferably from about 100,000 to about 1,500,000. The viscosity can be measured by means of a glass capillary viscometer as set forth in Dow Corning Corporate Test Method
15 CTM0004, July 20, 1970, which is incorporated by reference herein in its entirety. Silicone polymer of high molecular weight may be made by emulsion polymerization. Suitable silicone fluids include polyalkyl siloxanes, polyaryl siloxanes, polyalkylaryl siloxanes, polyether siloxane copolymers, and mixtures thereof. Other nonvolatile silicone polymers having hair conditioning properties
20 can also be used.

The silicone polymers herein also include polyalkyl or polyaryl siloxanes with the following structure (I)



30 wherein R is alkyl or aryl, and x is an integer from about 7 to about 8,000. "A" represents groups which block the ends of the silicone chains. The alkyl or aryl groups substituted on the siloxane chain (R) or at the ends of the siloxane chains (A) can have any structure as long as the resulting silicone remains fluid at room temperature, is dispersible, is neither irritating, toxic nor otherwise harmful when
35 applied to the hair, is compatible with the other components of the composition, is chemically stable under normal use and storage conditions, and is capable of being deposited on and conditions the hair. Suitable A groups include hydroxy,

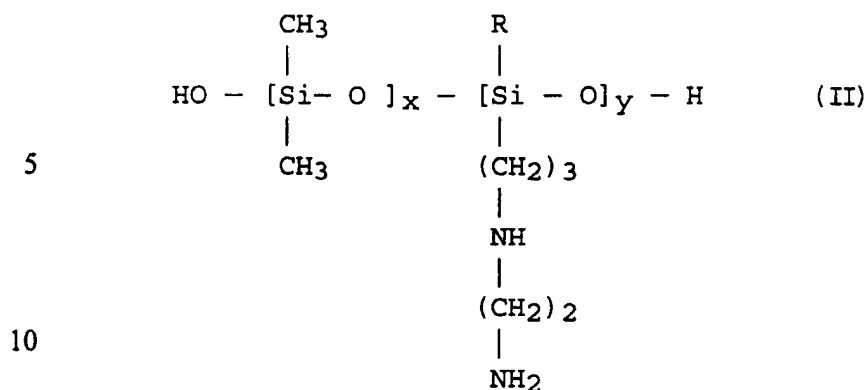
methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on the silicon atom may represent the same group or different groups. Preferably, the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicone polymers are polydimethylsiloxane, polydiethylsiloxane, and polymethylphenylsiloxane. Polydimethylsiloxane, which is also known as Dimethicone, is especially preferred. The polyalkylsiloxanes that can be used include, for example, polydimethylsiloxanes. These silicone polymers are available, for example, from the General Electric Company in their ViscasilR and SF 96 series, and from Dow Corning in their Dow Corning 200 series.

Polyalkylaryl siloxane fluids can also be used and include, for example, polymethylphenylsiloxanes. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade Fluid.

Especially preferred, for enhancing the shine characteristics of hair, are highly arylated silicone polymers, such as highly phenylated polyethyl silicone having refractive index of about 1.46 or higher, especially about 1.52 or higher. When these high refractive index silicone polymers are used, they should be mixed with a spreading agent, such as a surfactant or a silicone resin, as described below to decrease the surface tension and enhance the film forming ability of the material.

The silicone polymers that can be used include, for example, a polypropylene oxide modified polydimethylsiloxane although ethylene oxide or mixtures of ethylene oxide and propylene oxide can also be used. The ethylene oxide and polypropylene oxide level should be sufficiently low so as not to interfere with the dispersibility characteristics of the silicone. These material are also known as dimethicone copolyols.

Other silicone polymers include amino substituted materials. Suitable alkylamino substituted silicone polymers include those represented by the following structure (II)

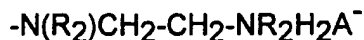
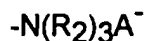
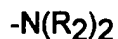
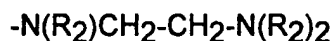


wherein R is CH₃ or OH, x and y are integers which depend on the molecular weight, the average molecular weight being approximately between 5,000 and 10,000. This polymer is also known as "amodimethicone".

Suitable amino substituted silicone fluids include those represented by the formula (III)

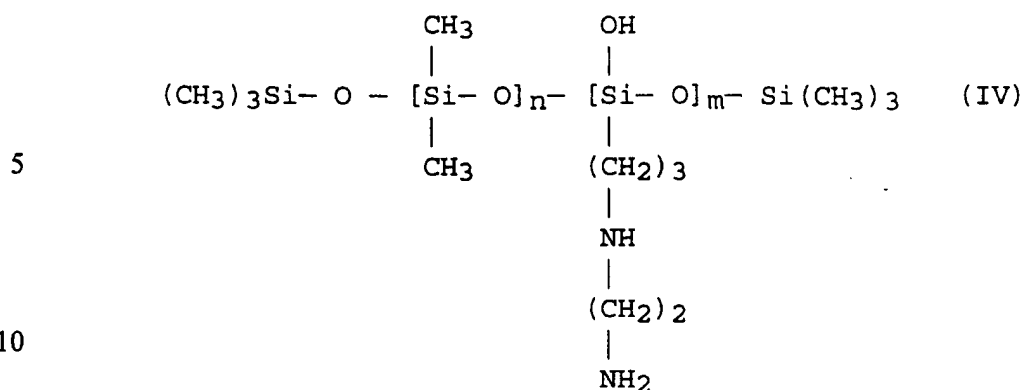


in which G is chosen from the group consisting of hydrogen, phenyl, OH, C₁-C₈ alkyl and preferably methyl; a denotes 0 or an integer from 1 to 3, and preferably equals 0; b denotes 0 or 1 and preferably equals 1; the sum n+m is a number from 1 to 2,000 and preferably from 50 to 150, n being able to denote a number from 0 to 1,999 and preferably from 49 to 149 and m being able to denote an integer from 1 to 2,000 and preferably from 1 to 10; R₁ is a monovalent radical of formula C_qH_{2q}L in which q is an integer from 2 to 8 and L is chosen from the groups



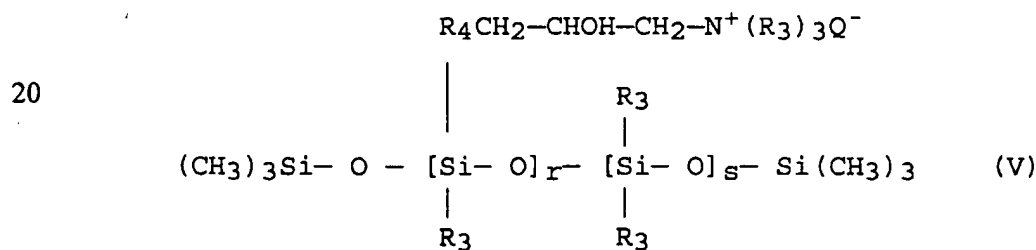
in which R₂ is chosen from the group consisting of hydrogen, phenyl, benzyl, a saturated hydrocarbon radical, preferably an alkyl radical containing from 1 to 20 carbon atoms, and A⁻ denotes a halide ion.

An especially preferred amino substituted silicone corresponding to formula (III) is the polymer known as "trimethylsilylamodimethicone", of formula (IV):



In this formula n and m are selected depending on the exact molecular weight of the compound desired.

Other amino substituted silicone polymers which can be used are represented by the formula (V):



where R^3 denotes a monovalent hydrocarbon radical having from 1 to 18 carbon atoms, preferably an alkyl or alkenyl radical such as methyl; R_4 denotes a hydrocarbon radical, preferably a $\text{C}_1 - \text{C}_{18}$ alkylene radical or a $\text{C}_1 - \text{C}_{18}$, and more preferably $\text{C}_1 - \text{C}_8$, alkyleneoxy radical; Q^- is a halide ion, preferably chloride; r denotes an average statistical value from 2 to 20, preferably from 2 to 8; s denotes an average statistical value from 20 to 200, and preferably from 20 to 50. A preferred polymer of this class is available from Union Carbide under the name "UCAR SILICONE ALE 56."

References disclosing suitable nonvolatile dispersed silicone polymers include U.S. Patent No. 2,826,551, to Geen; U.S. Patent No. 3,964,500, to Drakoff, issued June 22, 1976; U.S. Patent No. 4,364,837, to Pader; and British Patent No. 849,433, to Woolston, all of which are incorporated herein by reference in their entirety. Also incorporated herein by reference in its entirety is "Silicon Compounds" distributed by Petrarch Systems, Inc., 1984. This

reference provides an extensive, though not exclusive, listing of suitable silicone polymers.

Another nonvolatile dispersed silicone that can be especially useful is a silicone gum. The term "silicone gum", as used herein, means a polyorganosiloxane material having a viscosity at 25°C of greater than or equal to 1,000,000 centistokes. It is recognized that the silicone gums described herein can also have some overlap with the above-disclosed silicone polymers. This overlap is not intended as a limitation on any of these materials. Silicone gums are described by Petrarch, and others including U.S. Patent No. 4,152,416, to Spitzer et al., issued May 1, 1979 and Noll, Walter, Chemistry and Technology of Silicones, New York: Academic Press 1968. Also describing silicone gums are General Electric Silicone Rubber Product Data Sheets SE 30, SE 33, SE 54 and SE 76. All of these described references are incorporated herein by reference in their entirety. The "silicone gums" will typically have a mass molecular weight in excess of about 200,000, generally between about 200,000 and about 1,000,000. Specific examples include polydimethylsiloxane, poly(dimethylsiloxane methylvinylsiloxane) copolymer, poly(dimethylsiloxane diphenylsiloxane methylvinylsiloxane) copolymer and mixtures thereof.

Also useful are silicone resins, which are highly crosslinked polymeric siloxane systems. The crosslinking is introduced through the incorporation of tri-functional and tetra-functional silanes with mono-functional or di-functional, or both, silanes during manufacture of the silicone resin. As is well understood in the art, the degree of crosslinking that is required in order to result in a silicone resin will vary according to the specific silane units incorporated into the silicone resin. In general, silicone materials which have a sufficient level of trifunctional and tetrafunctional siloxane monomer units, and hence, a sufficient level of crosslinking, such that they dry down to a rigid, or hard, film are considered to be silicone resins. The ratio of oxygen atoms to silicon atoms is indicative of the level of crosslinking in a particular silicone material. Silicone materials which have at least about 1.1 oxygen atoms per silicon atom will generally be silicone resins herein. Preferably, the ratio of oxygen:silicon atoms is at least about 1.2:1.0. Silanes used in the manufacture of silicone resins include monomethyl-, dimethyl-, trimethyl-, monophenyl-, diphenyl-, methylphenyl-, monovinyl-, and methylvinylchlorosilanes, and tetrachlorosilane, with the methyl substituted silanes being most commonly utilized. Preferred resins are offered by General

Electric as GE SS4230 and SS4267. Commercially available silicone resins will generally be supplied in a dissolved form in a low viscosity volatile or nonvolatile silicone fluid. The silicone resins for use herein should be supplied and incorporated into the present compositions in such dissolved form, as will be
5 readily apparent to those skilled in the art. Without being bound by theory, it is believed that the silicone resins can enhance deposition of other silicone polymers on the hair and can enhance the glossiness of hair with high refractive index volumes.

Other useful silicone resins are silicone resin powders such as the
10 material given the CTFA designation polymethylsilsequioxane, which is commercially available as TospearlTM from Toshiba Silicones.

The method of manufacturing these silicone polymers, can be found in Encyclopedia of Polymer Science and Engineering, Volume 15, Second Edition, pp 204-308, John Wiley & Sons, Inc., 1989, which is incorporated herein by
15 reference in its entirety.

Silicone materials and silicone resins in particular, can conveniently be identified according to a shorthand nomenclature system well known to those skilled in the art as the "MDTQ" nomenclature. Under this system, the silicone is described according to the presence of various siloxane monomer units which
20 make up the silicone. Briefly, the symbol M denotes the mono-functional unit $(\text{CH}_3)_3\text{SiO}_{1.5}$; D denotes the difunctional unit $(\text{CH}_3)_2\text{SiO}$; T denotes the trifunctional unit $(\text{CH}_3)\text{SiO}_{1.5}$; and Q denotes the quadri- or tetra-functional unit SiO_2 . Primes of the unit symbols, e.g., M', D', T', and Q' denote substituents other than methyl, and must be specifically defined for each occurrence. Typical
25 alternate substituents include groups such as vinyl, phenyl, amino, hydroxyl, etc. The molar ratios of the various units, either in terms of subscripts to the symbols indicating the total number of each type of unit in the silicone, or an average thereof, or as specifically indicated ratios in combination with molecular weight, complete the description of the silicone material under the MDTQ system.
30 Higher relative molar amounts of T, Q, T' and/or Q' to D, D', M and/or M' in a silicone resin is indicative of higher levels of crosslinking. As discussed before, however, the overall level of crosslinking can also be indicated by the oxygen to silicon ratio.

Th silicone resins for use herein which are preferred are MQ, MT, MTQ,
35 MQ and MDTQ resins. Thus, the preferred silicone substituent is methyl.

Especially preferred are MQ resins wherein the M:Q ratio is from about 0.5:1.0 to about 1.5:1.0 and the average molecular weight of the resin is from about 1000 to about 10,000.

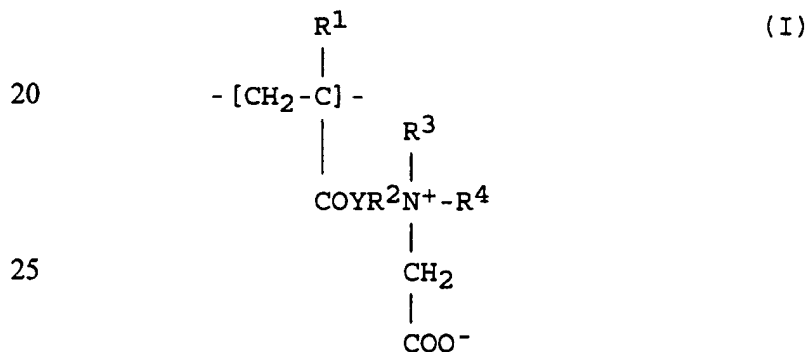
Hair fixative Polymer

5 The hair fixative polymer useful herein is one which provides hair fixative properties to the hair and is selected from the group consisting of amphoteric hair fixative polymers, anionic hair fixative polymers, and mixtures thereof. The hair spray and mousse compositions of the present invention typically include by weight from about 0.01% to about 10%, preferably from about 0.1% to about 5%
10 of a hair fixative polymer.

Amphoteric Hair Fixative Polymer

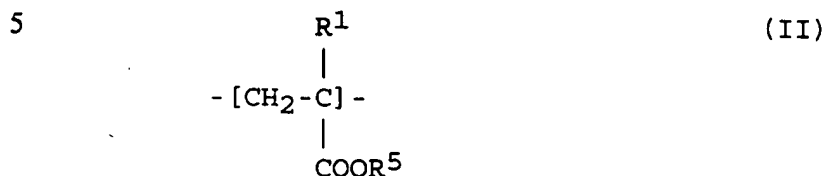
The amphoteric hair fixative polymers useful herein include the following polymers (1) to (5).

(1) Useful herein are polymers of betainised dialkylaminoalkyl (meth)acrylate or dialkylaminoalkyl (meth)acrylamide containing at least units of
15 the formula:



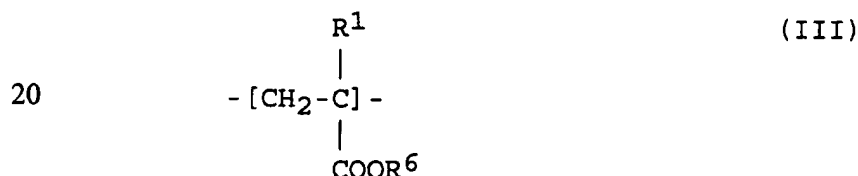
wherein R^1 denotes a hydrogen atom or a methyl group, R^2 denotes an alkylene group having 1 to 4 carbon atoms, Y denotes O or -NH- and R^3 and R^4
30 independently of one another denote hydrogen or alkyl having 1 to 4 carbon atoms, and one cationic derivative consisting of a cationic surfactant containing at least one nitrogen atom joined to one or more fatty chains and optionally quaternised, or consisting of a cationic polymer of the polyamine,
35 polyaminopolyamide or poly-(quaternary ammonium) type, the amine or ammonium groups forming part of the polymer chain or being joined thereto. These polymers usually have a molecular weight of 500 to 2,000,000.

The amphoteric polymers containing units corresponding to the above formula (I) are generally in the form of copolymers which contain, in addition to the units of the above mentioned formula (I), at least units of the formula:



wherein R^1 is as defined above and R^5 represents an alkyl or alkenyl radical having from 4 to 24 carbon atoms or a cycloalkyl radical having from 4 to 24 carbon atoms.

15 It is also possible to use terpolymers, tetrapolymers or pentapolymers which contain, in addition to the units (I) and (II) defined above, units of the formula:



25 wherein R^6 preferably denotes an alkyl or alkenyl group having 1 to 3 carbon atoms and R^1 is as defined above.

The units of the formula (I) are preferably present in an amount of 25 to 45% by weight, units of the formula (II) are preferably present in an amount of 5 to 65% by weight, and units of the formula (III) are preferably present in an amount up to 50% by weight, relative to the total weight of the polymer.

30 A particularly preferred polymer is the copolymer containing units of the formulae (I), (II) and (III) in which Y denotes an oxygen atom, R^2 denotes the group $-\text{C}_2\text{H}_4-$, R^1 , R^3 and R^4 denote methyl, R^5 denotes an alkyl group having 4 to 18 carbon atoms and R^6 denotes an alkyl group having 1 to 3 carbon atoms. The average molecular weight of this polymer is preferably from 70,000 to 90,000. This polymer is sold under the trademark "Yukaformer" or "Diaformer" supplied by Mitsubishi Chemical Corporation.

35

(2) Useful herein are the polymers resulting from the copolymerisation of a vinyl monomer carrying a carboxyl group, such as acrylic acid, methacrylic acid, maleic acid or alphachloroacrylic acid, and a basic monomer which is a substituted vinyl compound containing at least one basic nitrogen atom, such as dialkylaminoalkyl methacrylates and acrylates and dialkylaminoalkylmethacrylamides and -acrylamides.

(3) Useful herein are the polymers containing units derived from

i) at least one monomer chosen from amongst acrylamides or methacrylamides substituted on the nitrogen by an alkyl radical,

10 ii) at least one acid comonomer containing one or more reactive carboxyl groups, and

15 iii) at least one basic comonomer, such as esters, with primary, secondary and tertiary amine substituents and quarternary ammonium substituents, of acrylic and methacrylic acids, and the product resulting from the quaternisation of dimethylaminoethyl methacrylate with dimethyl or diethyl sulphate.

The N-substituted acrylamides or methacrylamides which are most particularly preferred are the groups in which the alkyl radicals contain from 2 to 12 carbon atoms, especially N-ethylacrylamide, N-tert.-butylacrylamide, N-tert.-octylacrylamide, N-octylacrylamide, N-decylacrylamide and N-dodecylacrylamide and also the corresponding methacrylamides. The acid comonomers are chosen more particularly from amongst acrylic, methacrylic, crotonic, itaconic, maleic and fumaric acids and also the alkyl monoesters of maleic acid or fumaric acid in which alkyl has 1 to 4 carbon atoms.

25 The preferred basic comonomers are aminoethyl, butylaminoethyl, N,N'-dimethylaminoethyl and N-tert.-butylaminoethyl methacrylates.

(4) Useful herein are the crosslinked and alkylated polyaminoamides partially or totally derived from polyaminoamides of the general formula:



30 wherein R represents a divalent radical derived from a saturated dicarboxylic acid, from a monocarboxylic or dicarboxylic aliphatic acid with an ethylenic double bond, or from an ester of a lower alkanol having 1 to 6 carbon atoms and of these acids or of a radical derived from the addition of any one of the said acids onto a bis-primary or bis-secondary amine, and Z denotes a radical of a bis-primary or mono- or bis-secondary polyalkylene-polyamine, and preferably
35 represents:

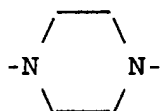
i) in proportions of 60 to 100 mol %, the radical



wherein x is 2 and N is 2 or 3 or alternatively x is 3 and n is 2, this radical being derived from diethylenetriamine, triethylenetetramine or dipropylenetriamine;

5 ii) in proportions of 0 to 40 mol %, the above radical (II) wherein x is 2 and n is 1 and which is derived from ethylenediamine, or the radical

10



derived from piperazine; and

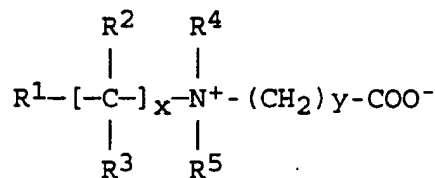
15 iii) in proportions of 0 to 20 mol %, the radical $-\text{NH}-(\text{CH}_2)_6\text{-NH}-$, derived from hexamethylenediamine, these polyaminoamides being crosslinked by the addition of a difunctional crosslinking agent chosen from amongst epihalogenohydrins, diepoxides, dianhydrides, and bis-unsaturated derivatives, using 0.025 to 0.35 mol of crosslinking agent per amine group of the polyaminoamide, and being alkylated by reaction with acrylic acid, chloroacetic acid or an alkane-sultone or their salts.

20 The saturated carboxylic acids are preferably chosen from amongst acids having 6 to 10 carbon atoms, such as adipic acid, 2,2,4- and 2,4,4-trimethyladipic acids, terephthalic acid and acids with an ethylenic double bond, such as acrylic, methacrylic and itaconic acids.

25 The alkane-sultones used in the alkylation are preferably propane- or butane-sultone, and the salts of the alkylating agents are preferably the sodium or potassium salts.

(5) Useful herein are the polymers containing zwitterionic units derived from the formula:

30



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wherein R^1 denotes a polymerisable unsaturated group, such as an acrylate, methacrylate, acrylamide or methacrylamide group, x and y independently

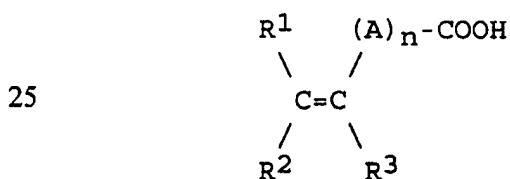
represent an integer from 1 to 3, R^2 and R^3 independently represent hydrogen, methyl, ethyl or propyl, and R^4 and R^5 independently represent a hydrogen atom or an alkyl radical such that the sum of the carbon atoms in R^4 and R^5 does not exceed 10.

5 Highly preferred amphoteric hair fixative polymers include commercially available material such as octylacrylamine/acrylates/butylaminoethyl methoacrylate copolymers with the tradenames; AMPHOMER, AMPHOMER LV71, AMPHOMER SH701, and AMPHOMER LV47 supplied by National Starch & Chemical, and methoacryloyl ethylbetaine/acrylates copolymers with the
10 tradenames; YUKAFORMER SM, YUKAFORMER 301, YUKAFORMER 510, YUKAFORMER M-75, YUKAFORMER FH, and YUKAFORMER R250S supplied by Mitsubishi Chemical Corporation.

Anionic Hair Fixative Polymer

15 The anionic hair fixative polymers useful herein include polymers containing units derived from carboxylic, sulphonic or phosphoric acid and usually have a molecular weight of 500 to 5,000,000. These polymers are water-soluble polymers, it being possible for this solubility to be obtained by neutralisation.

20 The carboxylic acid groups can be provided by unsaturated monocarboxylic or dicarboxylic acids, such as those corresponding to the formula:



30 wherein n is 0 or an integer from 1 to 10, A denotes a methylene group optionally joined to the carbon atom of the saturated group, or to the adjacent methylene group in the case where n is greater than 1, via a heteroatom, such as oxygen or sulphur, R^1 denotes a hydrogen atom or a phenyl or benzyl group, R^2 denotes a hydrogen atom, a lower alkyl group or a carboxyl group and R^3 denotes a hydrogen atom, a lower alkyl group, CH_2COOH , or a phenyl or benzyl group.

35 According to the invention, the preferred polymers containing carboxylic acid groups are:

(1) Homopolymers or copolymers of acrylic or methacrylic acid or salts thereof, and in particular, the products sold under the name VERSICOL E or K, and ULTRAHOLD by BASF and under the name DARVAN No. 7 by Van der Bilt; acrylic acid/acrylamide copolymers sold in the form of their sodium salt under the
5 name RETEN 421, 423 or 425 by HERCULES; and the sodium salts of polyhydroxycarboxylic acids, sold under the name HYDAGEN F by HENKEL.

(2) Copolymers of acrylic or methacrylic acid with a monoethylenic monomer, such as ethylene, styrene, a vinyl or allyl ester or acrylic or methacrylic acid ester, optionally grafted onto a polyalkylene glycol, such as
10 polyethylene glycol, and optionally crosslinked. Other such copolymers contain an optionally N-alkylated and/or N-hydroxylated acrylamide unit in their chain, such as those sold under the name QUADRAMER 5 by American Cyanamid.

(3) Copolymers derived from crotonic acid, such as those containing, in their chain, vinyl acetate or propionate units and optionally other monomers such
15 as allyl or methallyl esters, a vinyl ether or a vinyl ester of a saturated linear or branched carboxylic acid with a hydrocarbon chain of at least 5 carbon atoms, if appropriate, for these polymers to be grafted and crosslinked, or also a vinyl, allyl or methallyl ester of an α - or β -cyclic carboxylic acid. Included in this class are those with the tradename RESYN 28-2930, 28-2913, and 28-1310 sold by
20 National Starch & Chemicals.

(4) Polymers derived from maleic, fumaric and itaconic acids or anhydrides with vinyl esters, vinyl ethers, vinyl halides, phenylvinyl derivatives, acrylic acid and its esters, such as those sold under the name GANTREZ A, SP, and ES by ISP. Other polymers included in this class are copolymers of maleic,
25 citraconic and itaconic anhydrides with an allyl or methallyl ester optionally containing an acrylamido or methacrylamido group, or with an α -olefine, acrylic or methacrylic acid ester, acrylic or methacrylic acid or vinylpyrrolidone unit in their chain; the anhydride groups can be monoesterified or monoamidified.

(5) Polyacrylamides containing carboxylate groups. Polymers comprising
30 sulphonic groups include polymers containing vinylsulphonic, styrenesulphonic, lignosulphonic or naphthalenesulphonic units. These polymers are chosen, in particular, from amongst:

i) Polyvinylsulphonic acid salts having a molecular weight of 1,000 to 100,000, and also copolymers with an unsaturated comonomer, such as acrylic

or methacrylic acid or an ester thereof and also substituted or unsubstituted acrylamide or methacrylamide, vinyl esters, vinyl ethers and vinylpyrrolidone.

ii) Polystyrenesulphonic acid salts, such as the sodium salt sold by National Starch & Chemicals under the name Flexan 500 and 130.

5 iii) Alkali metal or alkaline earth metal salts of sulphonic acids derived from lignin, and more particularly calcium lignosulphonates or sodium lignosulphonates, such as the product sold under the name Marasperse C-21 by American Can Co. and the C₁₀ to C₁₄ products sold by Avebene.

10 iv) Polymers containing salified alkyl naphthalenesulphonic acid units, such as the sodium salt under the name Darvan No. 1 by Van der Bilt.

The anionic hair fixative polymers herein which include anionic monomers are preferably utilised in at least partially neutralised form in order to aid shampoo removability of the liquid hair cosmetic compositions. In the compositions the neutralisation of a polymer may be achieved by use of an
15 inorganic base, preferably KOH. However organic base, preferably AMP (amino methyl propanol) and mixture of inorganic and organic base may also be used to effect the desired level of neutralisation in hair styling compositions. In total from about 50% to about 100%, preferably from about 70% to about 100%, most preferably from about 80% to about 100% of the acidic monomers of each
20 polymer utilised should be neutralised with base.

Any conventionally used base, organic or inorganic, may be used for neutralisation of acidic polymers provided they are utilised as specified herein. Hydroxides of alkali, alkaline earth and amino alcohols are suitable neutralisers.

25 Examples of suitable organic neutralizing agents which may be included in the compositions of the present invention include amines, especially amino alcohols such as 2-amino-2-methyl-1, 3-propanediol (AMPD), 2-amino-2-ethyl-1, 3-propanediol (AEPD), 2-amino-2-methyl-1-propanol (AMP), 2-amino-1-butanol (AB), monethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), monoisopropanolamine (MIPA), diisopropanolamine (DIPA), triisopropanolamine
30 (TIPA), dimethylsteramine (DMS) and amino methyl propanol (AMP) and mixtures thereof.

Preferred neutralising agents for use in hair care compositions of the present invention are potassium and sodium hydroxides.

Highly preferred anionic hair fixative polymers include commercially
35 available material such as vinyl acetate/crotonic acid/vinyl neodecanoate

copolymers and vinyl acetate/crotonic acid copolymers with the tradenames RESYN 28-2930, RESYN 28-2913, and RESYN 28-1310 supplied by National Starch & Chemicals, and acrylates copolymers and acrylates/acrylamide copolymers with tradenames LUVIMER 100P, ULTRAHOLD 8, and
5 ULTRAHOLD STRONG supplied by BASF Corporation.

AQUEOUS CARRIER

The hair care composition of the present invention comprises an aqueous carrier. The level and species of the aqueous carrier are selected according to the compatibility with other components, and desired characteristic of the
10 product.

The aqueous carrier useful in the present invention include water and water solutions of lower alkyl alcohols, polyhydric alcohols, and mixtures thereof. The lower alkyl alcohol useful herein are alkyl monohydric alcohols having 1 to 4 carbons, preferably 2 or 3 carbons. The preferred low alkyl alcohol is ethanol,
15 isopropanol, and mixtures thereof. The polyhydric alcohols useful herein include propylene glycol, hexylene glycol, glycerin, propane diol, and mixtures thereof.

The water useful for the aqueous carrier include deionized water and water from natural sources containing mineral cations. Deionized water is preferred.

20 ADDITIONAL COMPONENTS

A variety of other additional components can be formulated into the hair care composition of the present invention. These additional components are selected by the artisan according to the desired characteristics of the final product. Such additional components generally are used individually at levels of
25 no more than about 5.0% by weight of the composition.

Additional components useful for shampoo and conditioning products are deterative surfactants such as anionic surfactants, nonionic surfactants, amphoteric surfactants and mixtures thereof; polyvalent metal cations such as Ca and Mg; suspending agents such as acyl derivatives, alkanol amides,
30 xanthan gum, and carboxyvinyl polymers; and stabilizing agents such as polyalkyleneglycol.

Additional components useful for hair styling products such as hair spray and mousse are cationic hair fixative polymers, nonionic hair fixative polymers, dispersing surfactants, and propellants such as dimethylether and LPG gas.

Cationic hair fixative polymers useful herein are: vinylpyrrolidone /
quaternized dialkylaminoalkyl acrylate or methacrylate copolymers; cellulose
ether derivatives containing quaternary ammonium groups; cationic
polysaccharides; cationic polymers containing quaternized units; polyamino-
5 polyamides prepared by the polycondensation of an acid compound with a
polyamine and their alkylated and/or crosslinked derivatives thereof; polyamino-
polyamide derivatives; polymers obtained by reacting polyalkylenepolyamine;
poly-(quaternary ammonium) compounds; homopolymers or copolymers derived
from acrylic or methacrylic acid; and polyalkyleneimines, condensates of
10 polyamines and of epichlorohydrin, poly-(quaternary ureylenes) and chitin
derivatives. Suitable cationic hair fixative polymers include commercially
available material such as Polyquaternium 4 under the tradenames CELQUAT
H100 and CELQUAT L200 supplied by National Starch & Chemicals, and
Polyquaternium 11 under the tradename GAFQUAT 755N supplied by ISP.

15 Nonionic hair fixative polymers useful herein are homopolymer of
vinylpyrrolidone or vinylcaprolactum and copolymers of vinylpyrrolidone with
vinylacetate such as those with tradenames LUVISKOL K grades and
LUVISKOL VA grades supplied by BASF Corporation.

Other additional components can be formulated into various product forms
20 of the present composition. These include: other conditioning agents such as
hydrolysed collagen, hydrolysed keratin, proteins, plant extracts, and nutrients;
preservatives such as benzyl alcohol, methyl paraben, propyl paraben and
imidazolidinyl urea, methylchloroisothiazoline, and methylisothiazoline; solvents
such as volatile and non-volatile silicone fluids of low molecular weight; pH
25 adjusting agents, such as citric acid, sodium citrate, succinic acid, phosphoric
acid, sodium hydroxide, sodium carbonate; salts, in general, such as potassium
acetate and sodium chloride; coloring agents, such as any of the FD&C or D&C
dyes; hair oxidizing (bleaching) agents, such as hydrogen peroxide, perborate
and persulfate salts; hair reducing agents such as the thioglycolates; perfumes;
30 sequestering agents, such as disodium ethylenediamine tetra-acetate; and
ultraviolet and infrared screening and absorbing agents such as octyl salicylate.

EXAMPLES

The following examples further describe and demonstrate embodiments
within the scope of the present invention. The examples are given solely for the
35 purpose of illustration and are not to be construed as limitations of the present

invention, as many variations thereof are possible without departing from the spirit and scope of the invention. Ingredients are identified by chemical or CTFA name, or otherwise defined below.

5 **EXAMPLE 1: Shampoo**

Component	Weight percent (%)
Polymer 1*1	1.00
Polyquaternium-10	0.50
Dimethicone	1.00
Ammonium lauryl sulfate	6.00
Ammonium laureth-3 sulfate	4.00
Cocamidopropyl betaine	4.00
Lauramide dimethanolamine	2.00
Methyl paraben	0.15
Propyl paraben	0.05
Perfume	0.50
Deionized Water	80.80

EXAMPLE 2: Conditioner

Component	Weight percent (%)
Polymer 1*1	1.00
Stearyltrimethylammonium chloride	2.00
Cetyl alcohol	2.00
Dimethicone	0.30
Cyclomethicone	1.70
EDTA	0.10
Benzyl alcohol	0.40
Perfume	0.20
Deionized Water	92.30

EXAMPLE 3: Hair spray

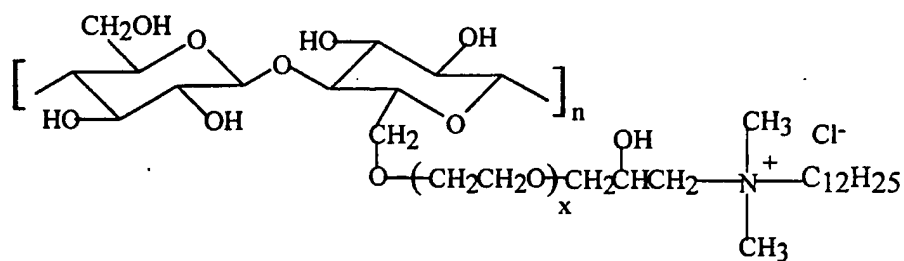
Component	Weight percent (%)
Polym r 1*1	1.00
Ultrahold 8 *2	2.00

Aminomethylpropanol	0.15
Perfume	0.10
Ethanol	25.00
Deionized Water	41.75
Propellant dimethylether	30.00

EXAMPLE 4: Mousse

Component	Weight percent (%)
Polymer 1 ^{*1}	2.00
Yukaformer SM ^{*3}	5.00
Polyoxyethylene (10) lauryl ether	0.25
Methyl paraben	0.15
Phenoxyethanol	0.25
Propylene glycol	0.10
Disodium EDTA	0.10
Perfume	0.05
Ethanol	5.00
Deionized Water	79.10
Propellant LPG gas	8.00

^{*1} Polymer 1: Hydrophobically modified cationic cellulose having the following
5 formula



$$x = 3$$

$$n = 60$$

10

^{*2} Ultrahold 8: Terpolymer of acrylic acid, ethyl acrylate, and N-t-butyl acrylamide supplied by BASF.

^{*3} Yukaformer SM: Methoacryloyl ethyl betaine / acrylates copolymer supplied by Mitsubishi Chemical Corporation

Method of Preparation

Examples 1 through 4 as shown above can be prepared by any conventional method well known in the art. Suitable methods are described below.

- 5 The shampoo of Example 1 is suitably made as follows: A silicone emulsion is made with Dimethicone, a small amount of deterative surfactant, and a portion of water. Separately, Polymer 1 and remaining deterative surfactants are dispersed in remaining water to form a homogeneous mixture. To this mixture is added other components except for the silicone emulsion and
10 perfume, and agitated. The obtained mixture is passed through a heat exchanger to cool, and the silicone emulsion and perfume are added.

- The conditioner of Example 2 is suitably made as follows: Water and stearyltrimethylammonium chloride are mixed at a temperature above 70°C. Then cetyl alcohol and benzyl alcohol are added with agitation. After cooling
15 down below 60°C, the remaining components are added with agitation, then cooled down to about 30°C.

- The hair spray of Example 3 is suitably made as follows: Ultrahold 8 is neutralized with aminomethylpropanol in a portion of water and ethanol. To this is added the remaining components except Polymer 1. Finally, Polymer 1 is
20 added, and the obtained mixture is mixed until homogeneous. The concentrate thus obtained is packed into an aerosol can with dimethylether.

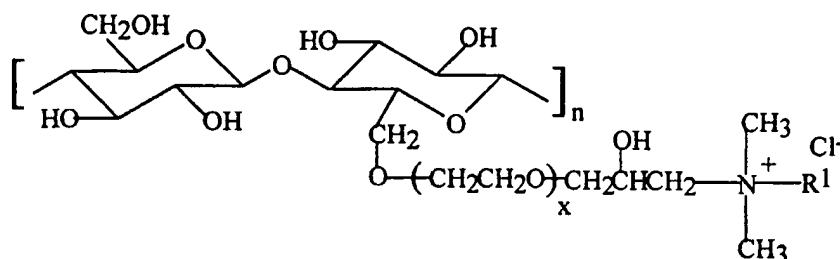
- The mousse of Example 4 is suitably made as follows: Yukaformer AM is dissolved in a portion of water. To this is added the remaining ingredients except Polymer 1. Finally, Polymer 1 is added, and the obtained mixture is mixed until
25 homogeneous. The concentrate thus obtained is packed into an aerosol can with LPG gase.

The hair care compositions of Examples 1 through 4 have many advantages. For example, they can provide softness, smoothness, slick feel, and ease of combing to the hair.

What is claimed is:

1. A hair care composition comprising by weight:

(a) from about 0.01% to about 10% of a hydrophobically modified cationic cellulose having the following formula:



5

wherein R¹ is an alkyl having from about 8 to about 22 carbons, n is an integer from 1 to about 1250; x is 0 or an integer from 1 to about 6; and having a molecular weight of no more than about 250,000;

10 (b) from about 0.01% to about 20% of a viscosifying agent selected from the group consisting of a gel network, a conditioning polymer, a hair fixative polymer, and mixtures thereof; and

(c) an aqueous carrier.

2. The hair care composition according to Claim 1 wherein the hydrophobically modified cationic cellulose has a molecular weight of about 800 to about 100,000.

3. The hair care composition according to Claim 1 wherein the 3% aqueous solution of the hydrophobically modified cationic cellulose has a viscosity of no more than about 200cps.

4. The hair care composition according to any of Claims 1 through 3 comprising by weight from about 0.1% to about 10% of the conditioning polymer selected from the group consisting of a cationic polymer, a nonionic polymer, a silicone polymer, and mixtures thereof.

5. The hair care composition according to Claim 4 comprising by weight from about 0.1% to about 19.9% of the gel network consisting of a solid aliphatic compound and a cationic surfactant.

6. The hair care composition according to any of Claims 1 through 3 comprising by weight from about 0.1% to about 10% of the hair fixative polymer selected from the group consisting of an amphoteric hair fixative polymer, an anionic hair fixative polymer, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/12281

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 288 484 A (TASHJIAN ANNE) 22 February 1994 see column 1, line 41 - column 3, line 27 see column 5, line 52 - line 64 ---	1,2,4
X	EP 0 686 388 A (KAO CORP) 13 December 1995 see page 2, line 25 - line 52 see page 3, line 18 - page 6, line 52 see page 7, line 11 - line 13 ---	1,4,5
X	DE 196 29 248 A (KAO CORP) 23 January 1997 see page 2, line 31 - page 3, line 33 see page 3, line 64 - page 4, line 25 ---	1,3,6
X	FR 2 706 296 A (L'OREAL) 23 December 1994 see page 2, line 21 - page 4, line 25; examples -----	1,4

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

9 February 1998

Date of mailing of the international search report

27.02.98

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/12281

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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FR 2706296 A	23-12-94	WO 9428861 A	22-12-94